

DESCRIPTION

ONE-PACK TYPE CURING PASTE MATERIAL FOR USE IN MECHANICAL
FOAMING APPARATUS

5

TECHNICAL FIELD

The present invention relates to one-pack type curing
paste material for mechanical foaming apparatus, in more
detail, one-pack type curing paste material suitable for
10 producing a cured product with dense uniform closed-cells
by a method of mechanically mixing and dispersing a low-
pressure gas into a paste material to produce an expandable
material, followed by discharging and expanding the
expandable material, especially by using a mechanical
15 foaming apparatus suitable for performing the method.

BACKGROUND ART

Until now, there is known a certain method for
producing a foamed product by mechanically mixing and
dispersing a low-pressure gas into a paste material to
20 produce an expandable material, followed by discharging and
expanding the expandable material (discharge and expansion
method), which comprises mechanically mixing and dispersing
said paste material and a low-pressure gas by using a
piston pump which is reciprocated in a cylinder to carry
25 out suction stroke and discharge stroke, by supplying a gas

into the cylinder during and/or after a suction stroke of a piston pump,

supplying a paste material into the cylinder with said gas by batch process,

5 carrying out the discharge stroke by using the piston pump after supplying the paste material, and

discharging the gas and the paste material to a pipe in the discharge stroke,

and then subjecting the resultant expandable material
10 to discharging and expanding,

as well as a mechanical foaming apparatus suitable for performing said method (see JP-B-3212533 (JP-A-10-272344)).

DISCLOSURE OF INVENTION

The above process is remarkably useful in the
15 standpoint to increase a safety in handling and a reliability of a gas injection and to control highly precisely the forming magnification. However, the cured product (foamed product) produced by the discharge and expansion method have sometimes continuous cells (i.e.,
20 ununiformity size foam) depending on the starting paste material, and hence, it has been desired to obtain always a constant-forming product with dense uniform closed-cells (i.e., uniform microcell).

Under the circumstances, the present inventors have
25 intensively studied, and as a result, have found that the

specification of viscosity characteristics of paste material make the above purpose achieve, and then the present invention has been completed.

That is to say, the present invention provides a method of discharging and expanding an expandable material to produce a cured product with dense uniform closed-cells,

comprising mechanically mixing and dispersing a low-pressure gas into a paste material to produce an expandable material, followed by discharging and expanding the expandable material,

wherein the paste material is a one-pack type curing paste material having viscosity characteristics included in the zone defined by points A, B, C and D in the graph of Fig. 1 showing the relationship between shear rate and apparent viscosity, said points A and B being at 50-30000 poises of an apparent viscosity (measured by a Brookfield rotary viscometer using spindle No.7, at 2 rpm, at 20°C) in low shear rate region (0.43 sec^{-1}) and said points C and D being at 20-2000 poises of an apparent viscosity (measured by an apparent viscosity meter according to JIS K2220 20°C) in high shear rate region (783 sec^{-1}). The present invention further provides a one-pack type curing paste material having the above viscosity characteristics which is useful in the above method.

The one-pack type curing paste material according to

the present invention is not limited by the kind of resin or the method of the curing, but should have the above viscosity characteristics, and especially the material is useful to be applied to the mechanical foaming apparatus
5 described in above-mentioned JP-B-3212533 (JP-A-10-272344).

With respect to the viscosity range mentioned above, when the apparent viscosity of 0.43 sec^{-1} is less than 500 poises, a foaming magnification decreases due to a foam collapse, on the other hand, when the apparent viscosity is
10 more than 30000 poises, an air leakage from the part around the discharge bead increases, which causes the forming magnification being 2-folds as much. Besides, when the apparent viscosity of 783 sec^{-1} is less than 20 poises, a foaming magnification decreases due to a cell collapse at
15 the discharge, and when the apparent viscosity is more than 2000 poises, the discharge becomes impossible since the liquidity of the materials becomes difficult.

In addition to such low/high shear rate, the apparent viscosity (measured by an apparent viscosity meter
20 according to JIS K2220 20°C) in middle shear rate region (64 sec^{-1}) is also set at the range of 27-3000 poises.

The one-pack type curing paste material refers to a material that is a one-pack type and a viscous paste state of high-viscosity at room temperature to heated temperature
25 before use, which has a curing mechanism based on curing by

a reaction, by cooling to room temperature from heated molten state, and by applying with thermal energy, light, radiation energy and the like. The examples of them are compositions of moisture-curable type, thermosetting type, 5 hot-melt type, sol-gel type, vulcanization-crosslinking type, and photo/radiation-curable type; said compositions comprising polyurethane resins, silicone resins, epoxy resins, synthetic rubbers, polyolefin resins, polyester resins, acrylic resins, poly(vinyl chlorides), or other 10 thermoplastics or thermoplastic elastomers; which can be prepared from a monomer, an oligomer, a polymer and the like of a thermoplastic and a thermosetting material.

In an embodiment, the one-pack type curing polyurethanes paste material comprising a urethane 15 prepolymer having a terminal active isocyanate group (NCO group); or a blocked urethane prepolymer and/or a blocked polyisocyanate compound which are temporarily blocked in order to inactivate the active isocyanate group of the urethane prepolymer and/or polyisocyanate compound. 20 Furthermore, the material comprises these urethane prepolymer as a main component and can be also prepared into a moisture-curable type; a thermosetting type in combination with a latent curing agent; or a thermosetting type comprising a normal curing 25 agent and/or a latent curing agent in combination with a

blocked polyisocyanate compound.

The urethane prepolymer including an active isocyanate group, which is used as polyurethanes paste material composed as above may be obtained by the reaction between
5 an excess amount of a polyisocyanate compound and a polyol.

The polyisocyanate compound includes aromatic, aliphatic and alicyclic polyisocyanate compounds, such as tolylene diisocyanate (TDI), diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,4-phenylene
10 diisocyanate, xylylene diisocyanate, tetramethylxylylene diisocyanate, naphthylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, crude TDI, polymethylene-polyphenyl isocyanate, isophorone diisocyanate, hexamethylene diisocyanate, xylylene diisocyanate hydride,
15 and isocyanurate, carbodiimide or biuret compounds of these isocyanate compounds, which may be used alone or in combination of one or more thereof.

The polyol component in the invention includes, for example,

20 polyether polyols which are made by addition-polymerization of an alkylene oxide such as ethylene oxide, propylene oxide, and a mixture of ethylene oxide and propylene oxide, with a polyhydric alcohol such as ethylene glycol, propylene glycol, glycerin, trimethylolpropane,
25 pentaerythritol, sorbitol, sucrose and the like;

ethylene glycol, propylene glycol, and oligoglycols thereof;

polyols such as butyleneglycol, hexyleneglycol, and polytetramethylene ether glycols;

5 polyester polyols such as polycaprolactone polyol and polyethylene adipate;

polyolefin polyols such as polybutadienepolyol, and polyisoprenepolyol;

10 higher fatty acid esters having hydroxyl group such as castor oil;

polysiloxane polyols having acryl polyol, and/or hydroxyl group(s); and

15 polymer polyols which are prepared by graft polymerization of polyether polyols or polyesters with a vinyl monomer.

The urethane prepolymer having a terminal active isocyanate group can be prepared by reacting a polyol component with an excess amount of the polyisocyanate compound in an equivalent ratio of 1.1-3.5 of the NCO group
20 of the polyisocyanate compound per the OH group of the polyol component. The reaction can be carried out at room temperature or heated temperature of 60-100°C for 1-24 hours in the presence of a catalyst (e.g. organic tin compound such as dibutyl tin dilaurate, bismuth compounds
25 such as bismuth octynoate, tertiary amine compounds, etc.).

Hence, a urethane prepolymer having a terminal active isocyanate (0.5-10% (w/w)) and a viscosity (3000-50000 centipoises/20°C) can be prepared.

The one-pack type curing polyurethanes paste material
5 may be made into a moisture-curable type which can be cured by reacting the active isocyanate group of urethane prepolymer with moisture of the atmosphere. For the moisture-curable type paste material, there may be used latent curing agent such as ketimine compounds, enamine
10 compounds, aldimine compounds, oxazolidine compounds and the like which are produced reversibly by a dehydration-condensation reaction of a polyamine compound and a carbonyl compound.

On the other hand, in order to make urethane
15 prepolymers into thermosetting type in combination with a latent curing agent can be activated by heat. The preferable latent curing agent is an inactivated solid polyamine. The solid polyamine at room temperature can preferably be produced, for example, by mixing 76.9 parts
20 by weight of 1,12-dodecanediamine (mp: 71°C) having a mean particle size of approximately 8 microns and 23.1 parts by weight of titanium oxide having a mean particle size of 0.02 microns; and milling the mixture with a jet mill to give a micronized polyamine having a mean particle size of
25 approximately 8 microns, which are adhered with titanium

oxide.

The procedure for producing the one-pack type curing polyurethanes paste material is described in detail in WO 95/26374 by the present inventors. The procedure is summarized below. The paste material is prepared by adding a latent curing agent of an inactivated solid polyamine to a single or mixture of a urethane prepolymer having a terminal active isocyanate group obtained by reacting a polyol with an excess amount of polyisocyanate compound, wherein said solid polyamine used as latent curing agent exhibits mp > 50°C and is for example, a micronized coated polyamine which is prepared by adhering a micronized powder having a mean particle size of 2 microns onto the surface of a solid polyamine having a mean particle size of about 20 microns whereby the active amino group of the polyamine is inactivated. The solid polyamine and micronized powder are used in the weight ratio of 1/0.001-0.5 (solid polyamine : micronized material) and whereby the amino groups of the surface is inactivated.

The solid polyamine used in the invention includes aromatic or aliphatic polyamine compounds having a melting point of not less than 50°C which is solid at room temperature, for example, aromatic solid polyamines such as 4,4'-diaminodiphenylmethane, 2,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane,

2,2'-diaminobiphenyl, 2,4'-diaminobiphenyl, 3,3'-diamino-
biphenyl, 2,4-diaminophenol, 2,5-diaminophenol, o-
phenylenediamine, m-phenylenediamine, 2,3-tolylenediamine,
2,4-tolylenediamine, 2,5-tolylenediamine, 2,6-tolylene-
5 diamine, 3,4-tolylenediamine and the like; and aliphatic
solid polyamines such as 1,12-dodecanediamine, 2,10-
decanediamine, 1,8-octanediamine, 1,14-tetradecanediamine,
1,16-hexadecanediamine and the like, which may be used
alone or in combination of two or more thereof. The solid
10 polyamines are grinded to be controlled to a mean particle
size of less than 20 μm , preferably 3-15 μm .

A method for inactivating the solid polyamine in the
latent curing agent is a coating of an amino group on the
particle surface with an inactivating agent. As the
15 inactivating agent, an organic or inorganic micronized
powder can be used, and it will be adhered on the particle
surface of a solid polyamine. The micronized powder also
includes an inorganic fine particle such as titanium oxide,
calcium carbonate, clay, silica, zirconia, carbon, alumina
20 and talc, and an organic fine particle such as poly(vinyl
chloride), polyacrylic resin, polystyrene and polyethylene.
The mean particle size of the micronized powder used herein
is not more than 2 microns, preferably not more than 1
micron. The inactivating procedure of a solid polyamine is
25 to cover the particle surface of the solid polyamine with

the above micronized powder. In the inactivating procedure, the weight ratio of solid polyamine powder/micronized powder ranges within about 1/0.001-0.5. During millling the solid polyamine so as to have a predetermined particle size, the micronized powder is mixed and dispersed thereto, so that the micronized powder can be adhered on the surface of the solid polyamine particles.

The urethane prepolymer and the inactivated solid polyamine latent curing agent prepared as mentioned above are blended in an equivalent ratio of the amino group of the polyamines to the isocyanate group of the urethane prepolymer being 1/0.5-2.0 when re-activated by heating.

The obtained one-pack type curing polyurethanes paste material can be cured by heating. Especially, the material exhibits critical curing characteristics in the heating temperature. When the temperature is less than 60°C, it is not cured, but when the temperature is 80°C or more, the inactivated solid polyamine will be re-activated and then the curing reaction initiates, which reaction will be almost completed within a very short time.

The blocked urethane prepolymer and/or blocked polyisocyanate compound used in the thermosetting type of one-pack type thermosetting polyurethanes paste material is produced by the blocking reaction wherein the active NCO group of the urethane prepolymer and/or polyisocyanate

compound can be provisionally inactivated with a blocker. The blocker includes phenols (phenol, cresol, xyleneol, ethylphenol and the like), lactams (ϵ -caprolactam, δ -valerolactam, β -butyrolactam, β -propiolactam and the like),
5 oximes (formamidoxime, acetoamidoxime, acetoxime, methylethylketoxime, diacetyl monoxime, benzophenonoxime, cyclohexanoneoxime and the like), activated methylenes (diethyl malonate, dimethyl malonate, ethyl acetoacetate, methyl acetoacetate, acetyl acetone and the like), alcohols
10 (methanol, ethanol, propanol, isopropanol, butanol, 2-ethylhexanol, ethyleneglycol monomethyl ether, ethyleneglycol monoethyl ether, ethyleneglycol monobutyl ether and the like), benzotriazole, mercaptans, acid amides, imides, amines, imidazoles, ureas and the like. In particular,
15 phenols, lactams and oximes are preferable. The blocking reaction of the NCO group of the urethane prepolymer or polyisocyanate compound with a blocker is carried out in an equivalent ratio of the active hydrogen group of the blocker to the NCO group of 0.9-1.1, in the presence of a
20 catalyst under heating temperature (50-110°C) to give a blocked urethane prepolymer or blocked polyisocyanate compound whose active NCO group is blocked.

The curing agent for the above blocked product includes the aforementioned active hydrogen compounds as a
25 polyol component for the preparation of the urethane

prepolymers, as well as a polyoxyalkylene polyamine, an alkylene oxide adduct of an aminoalcohol, an alkylene oxide adduct of an alkylene polyamine, a ketimine derivative of a polyoxy alkylene polyamine, a ketimine derivative of a polyamine and the like. The curing agent may be used in an amount of 0.5-1.5 equivalents to the active NCO group.

Examples of a filler for the one-pack type curing polyurethanes paste material having the above viscosity characteristics are ground calcium carbonate, treated calcium carbonate, clay, silica, zirconia, carbon, alumina, talc, mica, balloon, organic plastic balloon, plastic powder, plastic fiber, and the like. The paste material may optionally contain plasticizers (e.g., dibutyl phthalate, dioctyl phthalate, dicyclohexyl phthalate, diisooctyl phthalate, diisodecyl phthalate, dibenzyl phthalate, trioctyl phosphate, epoxy plasticizer, polyester plasticizer such as adipate), solvents, thixotropic agents, ultraviolet absorbers, antioxidants, adhesive promoters, dehydrating agents, foaming regulator, viscosity regulator and the like in a suitable amount.

In addition to the viscosity characteristics, other properties of a urethane prepolymer of a main ingredient may be tuned, for example, the thixotropic properties which are concerned with correlation between flow properties and structural viscosity are regulated by a kind, particle size

and amount of a filler; a surface-treated or non-treated filler; a kind and amount of a plasticizer; a viscosity regulator and the like.

More specifically, one-pack curing paste material of the present invention may be prepared in the following manner, first of all, polyether polyol and diphenyl methane diisocyanate can be reacted at the temperature of 80°C for 2 hours to give a urethane prepolymer having a terminal active isocyanate group (the amount of the terminal NCO group is 2.4 % and the viscosity is 100000 cps/20°C). An inactivated solid polyamine of a latent curing agent is prepared by mixing 76.9 parts by weight of 1,12-dodecanediamine (mp: 71°C) having a mean particle size of about 8 microns and 23.1 parts by weight of titanium oxide having a mean particle size of 0.02 microns and milling the mixture with a jet mill to give 100 parts by weight of the desired micronized coated polyamine having a mean particle size of about 8 microns. Next, to 100 parts by weight of the polyurethane prepolymer having the above terminal active isocyanate group, 2-10 parts by weight of a latent curing agent is added, and a filler is added in 0-100 parts by weight therein. When an opaque white or transparent foamed cured product is desired, any filler is not compounded, while when a rigid foamed cured product is desired, a large amount of fillers are compounded. In

order to obtain a composition having the desired viscosity characteristics of the present invention, a mixture of surface-treated calcium carbonate and untreated ground calcium carbonate is used as a filler. When a tough foamed
5 cured product is desired, a reinforcing filler such as carbon and silica is used. If the above reinforcing filler is incorporated in an amount of more than 50 parts by weight, the viscosity in low shear rate region increase and the thixotropic properties become strong, and then it may
10 not have the desired viscosity characteristics of the present invention. In order to avoid such a disadvantage, calcium carbonate should be added. When the particle size of calcium carbonate is small, the thixotropic viscosity characteristics are exhibited like incorporation of a
15 reinforcing filler, and then calcium carbonate having a particle size of more than 20 μm is used to adjust the viscosity characteristics. For example, when 10 parts by weight of ground calcium carbonate (average particle diameter: 45 μm), 10 parts by weight of calcium carbonate
20 treated with fatty acid (average particle diameter: 3 μm), 10 parts by weight of carbon as a filler are mixed with 20 parts by weight of a plasticizer, there is obtained a one-pack type thermosetting paste material having a lower shear rate region of 1000-5000 poise, a higher shear rate region
25 100-300 poise of paste material, a thermosetting critical

temperature of about 80°C. Optionally, silicone oil, nonionic surfactant may be compounded.

Next, in other embodiment, a silicone moisture-curable type material and a thermosetting type material are exemplified as a one-pack type curing silicones paste material. Organo-polysiloxane (silicone) having active hydroxy groups (silanols) at both ends and silanes or siloxanes compounds having two or more hydrolytic functional groups as a crosslinking agent are basic elements, which can be hydrolyzed with moisture of the media or the atmosphere and condensed to be cured. Especially, for the preparation of the thermosetting type paste material, a polysiloxane having a radical polymerized unsaturated double bond or a monomer, oligomer and/or polymer having no siloxane bond can be optionally used, and a polymerization initiator such as a peroxide compound is added to give a desired thermosetting type paste material. In this case, plasticizer, filler, coloring agent, adhesive promoter, promoting catalyst for curing reaction, foaming regulator, viscosity regulator and the like may be added for the preparation as the one-pack type curing polyurethanes paste material.

In order to exhibit a specific viscosity characteristics of the present invention, for example, 50-90 % (w/w) silicone, 2-10 % (w/w) crosslinking agent, 5-

50 % (w/w) filler may be added and further a small amount of a catalyst and adhesive promoter may be added if necessary. Particularly, a surfactant, a silicone oil and the like may be added to the one-pack type curing silicones paste material of the viscosity characteristics in order to make a low-pressure gas easily dispersed, to make the material desired expanded as a nearly spherical form and to prevent breaking foam or defoaming. Using a one-pack type curing silicones paste material, in particularly an opaque white or transparent cured product can be obtained.

Besides the above polyurethanes and silicones paste material, as a one-pack type curing paste material, a moisture-curing type material in which the main ingredient is a polyalkylene ether polymer having a terminal alkoxysilyl group, a vinyl polymer having a terminal alkoxysilyl group; or a thermosetting type may be used. The thermosetting type of the one-pack type curing paste material includes the above polyurethanes, silicones as well as unsaturated polyester resin and epoxy resin, furthermore crosslink of peroxide compound, crosslink of polyamine compound, crosslink of polyamide compound.

The photo/radiation-curable type of the one-pack type curing paste material includes UV-curable, photo-curable, electron-curable and the like, in which the main ingredient is a curable monomer and/or oligomer having a unsaturated

double bond(s), in which rubber, elastomer, the other polymer, photoreaction initiator and the like can be further added. Especially, the photo/radiation-curable type paste material is suitable for a transparent cured product. When the filler and the like is opaque, photo/radiation energy can be hardly penetrated to the paste material, so thereby it can be understood that the curable properties have disadvantageous.

The photo-curable monomer includes methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, trimethylolpropane triacrylate, trimethylolpropane triacrylate, methoxyethyl acrylate, n-butoxyethyl acrylate, dimethylaminoethyl acrylate, ethyleneglycol acrylate, neopentyl glycol acrylate, 1,6-hexanediol acrylate, diethylene glycol acrylate, triethylene glycol acrylate, dipropylene glycol diacrylate, ethylcarbitol acrylate, 1,5-pentanediol acrylate, pentane erythritol acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, benzyl acrylate, 2-hydroxyethyl acryloylphosphate, 2-hydroxy-3-phenoxypropyl acrylate, α,ω -diacryloyl bis-ethyleneglycol phthalate, α,ω -diacryloyl bis-ethylene glycol tetrahydrophthalate and the like.

The photo-curable oligomer includes epoxy acrylate

resin, urethane acrylate resin, polyester acrylate resin. The urethane acrylate resin is preferable due to its flexibility and elasticity after cured. The photo-curable oligomer is a base resin which may be a determinant for the characteristics of a cured product. The loadings of photo-curable monomer and/or oligomer used are 20-95% (w/w), preferably 30-90% (w/w).

The rubber, elastomer, and the other polymer include natural rubber, polyisoprene rubber, polyisobutylene rubber, polybutadiene rubber, butyl rubber, nitrilebutyl rubber, polychloroprene rubber, styrene butadiene rubber, styrene isoprene rubber, acryl rubber, polybutylene, polybutene, polyphenylene oxide, polycarbonate, vinyl polyacetate, methacryl resin, polyacrylonitrile, thermoplastic polyester, polyamide, polyvinyl butyral, epoxy resin, vinyl ethylene acetate copolymer and the like. These are used as a solution or a uniform dispersion of photo-curable monomer and/or oligomer.

The photoreaction initiator includes benzoin methyl ether, benzoin ethyl ether, α -methyl benzoin, benzophenone, benzyl, acetophenone, anthraquinone, phenanthroquinone, benzylsulfide, 2-chlorothioxanthone, 2-methylthioxanthone and the like. The photoreaction initiator is loaded in an amount of 1-7 parts, preferably 2-5 parts by weight to 100 parts by weight of the main ingredient. When necessary, a

polymerization inhibitor and so on can be loaded.

Furthermore, a hotmelt type of the one-pack type curing paste material has a mechanism wherein the solid at room temperature is heated to molten state and then solidified by cooling to room temperature, including a material comprising a thermoplastic resin, which is molten by heating and then solidified by cooling to room temperature. The thermoplastic resin includes polyethylene, polypropylene, polyolefin copolymers such as ethylene propylene copolymer, ethylene vinyl acetate copolymer and SEBS (styrene ethylene/butylene styrene), polystyrene, polyester resin, acrylic resin, poly(vinyl chloride), poly(vinylidene chloride), fluorine resin, polycarbonate, polyacetal, polyamide, styrenebutadiene, polybutadiene, and copolymer thereof. To these thermoplastic resins, a crosslinking functional group such as hydroxyl group, carboxyl group, glycidyl group, amino group, mercapto group, isocyanate group and alkoxysilyl group can be attached, and then the resulting resins can be combined with a compound having a functional group which is reacted with the above crosslinking functional group, to prepare a one-pack type curing paste material.

The sol-gel type refers to a one-pack type curing paste material of plastisols, and it is a sol-formed one-pack type curing paste material which can be provided by

dispersing a fine particle such as poly(vinyl chloride), acrylic resin and polyurethane resin in a plasticizer. This can be hardened from sol to gel by heating.

BRIEF DESCRIPTION OF DRAWINGS

5 Fig. 1. A graph that indicates the viscosity characteristics of the paste material of the present invention.

 Fig. 2. A circuit diagram of the mechanical foaming apparatus.

10 Fig. 3. A front cross-sectional view showing the structure of the piston pump.

 Fig. 4. A timing chart for illustrating an operation of the piston pump.

BEST MODE FOR CARRYING OUT THE INVENTION

15 The discharging and expanding method of a one-pack type curing paste material of the present invention is illustrated with reference of the drawings.

 Firstly, on carrying out the method of the discharge and expansion, for example, the mechanical foaming apparatus shown in Figure 2 is preferably used, which is
20 composed of a gas supplying device 10, a one-pack type curing paste material supplying device 11, a piston pump 12, a control device 13, a pressurizing device 14, a dispersing device 15 and a discharge device 16.

25 The gas supplying device 10 supplies a low-pressured

gas adjusted in a range of approximately 0.1-5 kg/cm², preferably 0.1-3 kg/cm².

This gas supplying device 10 comprises the port 31 for receiving compressed air from a compressor, a pressure regulating valve 34 and a gas flowmeter 35, etc. The compressed gas is not limited to compressed air, and therein carbon dioxide gas, nitrogen gas and the like may be also used.

The one-pack type curing paste material supplying device 11 supplies the one-pack type curing paste material PM to the pipe 39A under a high pressure adjusted in a range of approximately 100-300 kg/cm², preferably approximately 150-250 kg/cm². In this embodiment, the plunger pump 42A of a follower-plate type and the like is used as a pump for pumping the one-pack type curing paste material. With the plunger pump 42A, the one-pack type curing paste material PM filled in a container is transferred into pipe 39A under a high pressure.

The piston pump 12 comprises two piston pumps 45A and 45B which are alternately operated. The piston pumps 45A and 45B include pistons reciprocally and linearly moved by motors M2A and M2B respectively. Thus, the piston reciprocally moves within a cylinder in each piston pump, thereby effecting the suction stroke and the discharge stroke. The piston pumps 45A and 45B are laid between the

pipe 39A and the pipe 44A, and hereby the one-pack type curing paste material PM supplied under pressure from the paste material supplying device 11 and a gas supplied from the gas supplying device 10 are introduced under a predetermined pressure in a batchwise manner.

Then, the structure of the piston pumps 45A (and 45B) is illustrated with reference to Figure 3.

The piston pump 45A comprises a cylinder 451, a piston 452 which sealingly engages and slidably moves within the cylinder 451 and three needle valves NV1, NV3 and NV5 set in the cylinder 451.

The needle valve NV5 is a valve for controlling discharge, which is set at the stroke end of the discharge stroke in the piston pump 45A. The needle valve NV3 is a valve for controlling supply of the gas, which is set in the vicinity of the stroke end of the discharge stroke. The needle valve NV1 is a valve for controlling supply of the one-part type curing paste material PM, which is set in the vicinity of the stroke end of the suction stroke.

The needle valves NV1, NV3 and NV5 are substantially identical to each other in terms of structure. In each needle valve, the needle 453 is axially moved by a pneumatic cylinder so that the forward end of the needle 453 opens and closes the aperture 454 set on the inner circumferential surface or the end surface of the cylinder

451. The valve body includes the port 455 communicating with the valve chamber.

When the needle valves NV1, NV3 and NV5 are closed, the forward end of the needle 453 is same level on one side with the inner circumferential surface or the end surface of the cylinder 451, so that the dead space between the needle 453 and the piston 452 is substantially zero. Therefore, when the needle valves NV1, NV3 and NV5 are closed, there is no possibility that a part of the gas or the paste material supplied into the cylinder 451 will enter and remain in the valve chambers of the needle valves NV1, NV3 and NV5. When the needle valve NV5 opens to effect the discharge stroke, all the gas and the one-pack type curing paste material in the cylinder 451 are discharged.

The check valves CV3 and CV4 are set in the pipe 39B, and the check valves CV5 and CV6 are set in the pipe 44A, respectively. The volume (discharge volume) of the cylinder of each of the piston pumps 45A and 45B is determined from the diameter and stroke (the distance by which the piston moves) of the piston 452.

The control device 13 controls motors M1A, M2A and M2B and the needle valves NV1, NV3 and NV5 so as to supply the gas into the cylinder 451 of each of the piston pumps 45A and 45B during and/or after the suction stroke, supply the

one-pack type curing paste material PM into the cylinder 451 after the suction stroke and effect the discharge stroke after completion of the supply of the one-pack type curing paste material PM, thereby to discharge the gas and the one-pack type curing paste material into the pipe 44A.

Furthermore, now the way of the operations of the piston pumps will be illustrated based on the timing chart of Figure 4.

In either of the piston pumps 45A and 45B, the piston 452 moves from the discharge end to the suction end, thereby to effect the suction stroke. During the suction stroke, when the time T1 has passed after starting the movement of the piston 452, the needle valve NV1 opens, thereby to supply the gas into the cylinder. The time T1 is a period of about 1-2 seconds. During this period, the pressure in the cylinder 451 is negative. At a short time after the piston has reached the suction end, the needle valve NV1 closes. Therefore, at the time of completion of the suction stroke, the cylinder 451 is filled with the gas having the regulated pressure. When the amount of gas measured is less than a predetermined value, the control device 13 emits a warning signal. Thus, the supply amount of the gas during the suction stroke is monitored by the control device 13.

When the time T3 has passed after closing of the

needle valve NV1, the needle valve NV3 opens. The time T3 is a period of about 0.1-0.5 second. Thus, simultaneous opening of the needle valves NV1 and NV3 can be prevented. The needle valve NV3 is open for the time period T4.

5 During this period, the one-pack type curing paste material PM is supplied from the one-pack type curing paste material supplying device 11 into the cylinder 451. Due to high pressure of the one-pack type curing paste material, the low-pressure gas, which has been supplied to the cylinder
10 451 before supplying the one-pack type curing paste material, is compressed in a ratio equal to the pressure ratio of the gas to give the one-pack type curing paste material. Consequently, the volume of the gas becomes almost negligible.

15 For example, when the pressure of the low-pressure gas is 1 kg/cm^2 and the pressure of the one-pack type curing paste material is 200 kg/cm^2 , then the volume of the gas becomes about $1/200$. In this case, the one-pack type curing paste material in an amount equal to the volume of
20 the cylinder 451 is mixed with the gas of 1 kg/cm^2 in the same volume. It should be noted that the gas of 1 kg/cm^2 in a volume equal to the volume of the cylinder 451 is equivalent to the gas under atmospheric pressure (a pressure of 0 kg/cm^2) in a volume twice that of the
25 cylinder 451. That is, supplying the gas of 1 kg/cm^2 into

the cylinder is equivalent to pressurizing the cylinder to +1 kg/cm², as the pressure in the cylinder is a negative pressure of about -1 kg/cm² before supplying the gas during the suction stroke. Therefore, the mixing ratio R of the low-pressure gas and the one-pack type curing paste material when the volume of the gas is converted into that under atmospheric pressure is 2:1. The mixing ratio R is expressed by a general formula $R=(P_1+1):1$ wherein P_1 indicates the supply pressure of the low-pressure gas. That is, the mixing ratio R can be easily adjusted or controlled by adjusting the supply pressure P_1 of the low-pressure gas.

When the low-pressure gas is mixed with the one-pack type curing paste material and the mixture is dispersed, the one-pack type curing paste material is foamed upon discharge into the atmosphere in a volume 3 (=1+2) times that of the cylinder. In other words, a foaming ratio A of the one-pack type curing paste material is "3". The foaming ratio A is expressed by a general formula (P_1+2) wherein P_1 indicates the supply pressure of the low-pressure gas.

When the time T5 has passed after closing of the needle valve NV3, the needle valve NV5 opens, and the piston 452 moves from the suction end to the discharge end, thereby to effect the discharge stroke. The time T5 is

within a range of about 0.1-0.5 second. During the discharge stroke, the needle valves NV1 and NV3 are closed so that the forward end of the needle 453 of each of the needle valves NV1 and NV3 is same level on one side with the inner circumferential surface of the cylinder 451. Therefore, the dead space is zero and all the low-pressure gas and all the one-pack type curing paste material in the cylinder 451 are discharged from the aperture 454 of the needle valve NV5. When the time T6 has passed after completion of the discharge stroke, the subsequent suction stroke starts. The time T6 is within a range of about 0.1-0.5 second.

With respect to the piston pumps 45A and 45B, after the discharge stroke of one piston pump is completed, the discharge stroke of the other piston pump starts. Consequently, the piston pumps 45A and 45B alternately discharge a gas-mixed material (the best expandable material) into the pipe 44A. In the pipe 44A, the gas-mixed materials from the piston pumps 45A and 45B individually form two layers of the one-pack type curing paste material and the compressed low-pressure gas discharged by a single discharge stroke. Therefore, a series of two-layered materials are discontinuously arranged in the pipe 44A and the gas-mixed materials are arranged in a pulse-like manner in the pipe 44A. Such

state can make the subsequent dispersion succeed.

The pressurizing device 14 comprises: the piston pumps 51A, 51B, each comprising a piston reciprocally and linearly driven by a motor to pressurize a fluid; the on-off valves 52A, 52B, 53A and 53B; and the pressure sensors 55A and 55B.

The gas-mixed materials discharged into the pipe 44A are supplied by the piston pumps 51A and 51B which are alternately operated, and are transferred into the pipes 57A and 57B. For example, with respect to an operation of the piston pump 51A, when the piston moves upward within a cylinder while the on-off valve 52A is opened and the on-off valve 53A is closed, the gas-mixed material in the pipe 44A is suctioned into the cylinder. When the piston moves downward while the on-off valve 52A is closed and the on-off valve 53A is opened, the gas-mixed material in the cylinder is extruded to be in a pressurized state. The pressure in the cylinder is detected by the pressure sensor 55A, and thereby a detection signal is sent to the control device 13. The extrusion pressure of the piston pump 51A is 150 kg/cm^2 or more. The motor for driving the piston is controlled in accordance with a signal from the control device 13, thus controlling suctioning and extrusion of the piston pump 51A and the stream rate (the extrusion rate).

The dispersing device 15 (and the discharge device 16)

comprises the dispersing pipe 61 and the on-off valve 65, the discharge pipe 71, the discharge on-off valve 72 and the nozzle 73. The dispersing pipe 61 is a hose having a length of about 2-10 m. In the dispersing pipe 61, the pressure of the gas-mixed material is 150 kg/cm² or more, for example, 200-250 kg/cm². During passing of the pressurized gas-mixed material through the dispersing pipe 61, the gas is dispersed into the paste material PM in the form of fine bubbles having an average diameter of about 0.01 mm.

When the valve 72 is opened, the expandable material from the on-off valve 65 is discharged from the nozzle 73 under the atmospheric pressure. Upon discharge, the fine-dispersed low-pressure gas expands thereby to foam the one-pack type curing paste material. The expandable material whose forming magnification is 1.5-5 can be applied to foam-coating by moving the nozzle 73 on a predetermined trajectory.

The foam-coated one-pack type curing paste material can be left to stand (to cure in normal condition) or cured in an appropriate manner to give a cured product (foaming product) with dense uniform closed-cells.

The index of shape retention as to the foamed cell of the cured product indicates that the water absorption is not more than 10 % and the diameter of the closed-cell is

not more than 500 μm .

Example

The present invention is illustrated by the following Example.

5 Example 1

Under the above-mentioned discharge and expansion procedure,

10 a one-pack type curing paste material having the below viscosity characteristics and 1 kg/cm^2 of low-pressure gas were mechanically dispersed to give an expandable material, and this material was discharged, expanded, and then cured to give a cured product of closed-cells wherein the water absorption is 2-3 % and diameter of the cell is 50-100 μm .

one-pack type curing paste material*	apparent viscosity	
	(poises)	
	(0.43 sec^{-1})	(783 sec^{-1})
A. one-pack type thermosetting polyurethanes	2400	175
A ₁ . one-pack type thermosetting polyurethanes	60	28
A ₂ . one-pack type thermosetting polyurethanes	10000	1200
B. one-pack type moisture- curable polyurethanes	20000	400
C. one-pack type moisture- curable silicones	3000	600

*)

15 A. PENGUIN FOAM PU-A, produced by SANSTER GIKEN KABUSHIKI
KAISHA

A₁. PENGUIN FOAM PU-A₁, produced by SANSTER GIKEN KABUSHIKI
KAISHA

A₂. PENGUIN FOAM PU-A₂, produced by SANSTER GIKEN KABUSHIKI
KAISHA

B. PENGUIN FOAM PU-B, produced by SANSTER GIKEN KABUSHIKI
KAISHA

5 C. PENGUIN FOAM SR-C, produced by SANSTER GIKEN KABUSHIKI
KAISHA

INDUSTRIAL APPLICABILITY

From the above result, it has been found that a foamed
cured product with dense uniform closed-cells can be
10 produced from one-pack type curing paste material having
suitable viscosity characteristics, and the foamed cured
product thus prepared can be applied to various fields of
products requesting heat insulation, lightweighting, shock-
absorbing, cushioning, sound deadening, vibration damping,
15 impact-absorbing, protection, skin-decorating, waterstop
and airtight; for example, constructing and building
materials, packages, electric and electronic appliances,
automobiles, household articles, sport articles and
utensils.

20 Hence, the expandable materials of the present
invention can be used, for example, as a sealant, an
adhesive, a coating material, a gasket, a packing, a
cushion, an insulator, a foamed molded material, etc.